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Near Range Order Structural Information of Anodic Silver Oxide Layers by Means of Reflectivity Fine Structure Data Evaluation

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Abstract: Silver oxide (Ag₂O and AgO) layers were prepared by the anodic oxidation of silver metal in 1M NaOH and investigated in situ with XAFS at grazing incidence. For given glancing angles, x-ray absorption fine structure spectra of the anodic oxides were extracted from these reflectivity data. The evaluation of these absorption data yields detailed near range structural information about the electrochemically prepared oxides.

1. INTRODUCTION

In general, the determination of near range order structural information from reflectivity fine structure data cannot be performed straightforwardly because, in contrast to transmission XAFS, both the real and the imaginary part of the refractive index contribute to the reflectivity fine structure; i.e. the x-ray reflectivity fine structure cannot directly be compared with the XAFS theory. As recently shown, however, XAFS may be obtained from reflectivity fine structure data of homogeneous and isotropic media [1-3]. Furthermore, also the near range order structure of thin films can be deduced, if the penetration depth of x-rays is sufficiently smaller than the film thickness. The silver oxide films investigated in the present study were prepared by anodic oxidation of silver in 1M NaOH. For polarization potentials \( U_{\text{ref}} \) between 0.5 V \( \leq U_{\text{ref}} \leq 0.7 \) V, Ag₂O layers with a thickness of about 100 nm are formed, while above \( 0.75 \) V, AgO films with similar thicknesses are grown. Therefore, the anodic oxide layers can be considered as homogeneous media with respect to the penetration depth of x-rays which is about 3-10 nm for the chosen glancing angles \( \Theta (0.05^\circ \leq \Theta \leq 0.11^\circ) \), and the evaluation of the reflectivity XAFS data yields detailed near range order structural information representing the crystallographic properties of the oxide layers. Details about the applied mathematical procedure are given in ref. [2, 3]. The presented experiments were performed at the ROEMO II beamline at HASYLAB (Hamburg). The reflection mode XAFS data were collected in situ in the vicinity of the Ag-K edge at 25.514 keV in an electrochemical cell for several glancing angles below and above the critical angle of total external reflection. Further details of the experimental setup are given elsewhere [3, 4].

2. RESULTS AND DISCUSSION

Fig. 1 shows the Fourier-Transform magnitude (FT) of the \( k^2 \)-weighted XAFS data extracted from a reflectivity XAFS spectrum measured in situ at 0.09\(^\circ\) for an electrode potential \( U_e = 0.7 \) V. The peaks at about 0.15, 0.26, 0.32 and 0.39 nm correspond to the first four coordination shells of Ag₂O at 2.084, 0.334, 0.391 and 0.472 nm. While the information depth amounts to about 10 nm according to a penetration depth of the x-rays of \( \approx 3.4 \) nm, an Ag₂O thickness of about 70 nm was calculated from the electrochemical current. As expected no contributions from the underlying metal are detectable in this FT. The data in the range between 0.07 nm and 0.23 nm, representing the nearest neighbour peak, were backtransformed into k-space and fitted with phases and amplitudes calculated with FEFF [5]. The inverse Fourier-Transform of the peak as well as the fit line are depicted in the insert of Fig. 1. A single shell model with four parameters was applied: the interatomic distance \( R \), the coordination number \( N \), the root mean square deviation in the coordination distance \( \sigma \), and the inner potential shift \( \Delta E_p \). The fit results are compiled in Tab. 1. For comparison, parameters deduced from transmission XAFS data of polycrystalline Ag₂O are also listed. The values determined for the nearest neighbour distance and the related coordination number are close to the values expected from the crystallographic data \( R=0.204 \) nm, \( N=2 \). The disorder of the electrochemically formed silver (I) oxide is comparable to that of the polycrystalline Ag₂O reference compound. The strong increase of the inner potential shift \( \Delta E_p \) for the anodically grown silver oxide films can be related to the calculation procedure as follows. In general, the absorption edge position is defined by the first maximum of the derivative of an absorption spectrum [6]. In contrast to a transmission spectrum, a reflectivity spectrum is always depending on both \( \beta \) and \( \delta \) as a function of energy as already mentioned, and the shape of a reflectivity spectrum changes dramatically with \( \Theta \) (e.g. ref. [7]). Especially, a strong decrease of the edge position defined by the first maximum of the derivative of the reflectivity spectra is observed. Therefore these edge positions and also the resulting \( \Delta E_p \)-values can be expected to differ from those derived from transmission XAFS spectra. Furthermore, the energy resolution of the monochromator of about 12 eV at 25 keV photon energy may also have an influence to the determined \( \Delta E_p \)-values.
Tab. 1: Comparison of the crystallographic parameters of the first Ag-O shell determined from the evaluation of the reflectivity XAFS data of anodic silver oxide films formed at U\textsubscript{e}=+0.6 V and U\textsubscript{e}=+0.7 V and transmission XAFS data of polycrystalline Ag\textsubscript{2}O. In each case, the values are averaged over five individual measurements.

<table>
<thead>
<tr>
<th>Anodic silver oxide films</th>
<th>R / nm</th>
<th>N</th>
<th>σ / nm</th>
<th>ΔE\textsubscript{p} / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>U\textsubscript{e}=+0.6 V</td>
<td>0.195</td>
<td>2.016</td>
<td>0.0073</td>
<td>29.57</td>
</tr>
<tr>
<td>U\textsubscript{e}=+0.7 V</td>
<td>0.195</td>
<td>1.987</td>
<td>0.0088</td>
<td>28.27</td>
</tr>
<tr>
<td>Polycrystalline Ag\textsubscript{2}O</td>
<td>0.196</td>
<td>2.082</td>
<td>0.0077</td>
<td>7.96</td>
</tr>
</tbody>
</table>

In Fig. 2, the FT of XAFS data calculated from a reflectivity spectrum of an Ag-electrode oxidized at U\textsubscript{e}=+0.85 V is depicted. Due to the electrochemical Ag\textsubscript{2}O formation, one observes a splitting of the first Ag-O peak at about 0.15 nm. In crystalline Ag\textsubscript{2}O, Ag ions are existing in a dual valency, i.e. Ag\textsuperscript{+} ions are linearly coordinated with two oxygen ions at R\textsubscript{p}=0.218 nm while Ag\textsuperscript{2+} ions are coordinated in a square planar arrangement with four oxygens at R\textsubscript{p}=0.203 nm [8]. For the electrochemically prepared Ag\textsubscript{2}O-film in Fig. 2, a two shell parameter fit yields N\textsubscript{p}=3.2, R\textsubscript{p}=0.193 nm, N\textsubscript{p}=2.1 and R\textsubscript{p}=0.217 nm; i.e. the investigated Ag\textsubscript{2}O-film is highly oxygen deficient. The formation of an intermediate phase such as Ag\textsubscript{2}O\textsubscript{3} as proposed by Mansour [8] seems to be very likely during the electrochemical oxidation of Ag in alkaline media.

3. CONCLUSIONS

Detailed near range order structural information such as bond distances, coordination numbers and Debye-Waller factors of electrochemically prepared oxide films can be obtained from the evaluation of reflectivity fine structure data if the penetration depth of x-rays is sufficiently smaller than the film thickness. While results obtained for electrochemically prepared Ag\textsubscript{2}O layers are very close to those from transmission XAFS data of polycrystalline Ag\textsubscript{2}O, the structural parameters calculated for Ag\textsubscript{2}O-layers formed at more anodic potentials differ considerably from those of crystalline Ag\textsubscript{2}O.

References